Relation Between Fuel Properties and Chemical Composition.
IV.   Stability of Oil Shale Derived Jet Fuel

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INTRODUCTION

    The Navy has been interested in the utilization of alternate
fossil fuels for sometime (1). Our interest is focused primarily in
establishing the effects of chemical composition on fuel properties,
since such relations will lead to production efficiency and better
utilization of fuels. We recently reported some of our results
on jet fuels derived from coal, tar sands and oil shale (1a). Earlier
papers in this series report on other aspects of oil shale derived
fuels obtained from a large production experiment performed by Paraho,
Inc. (2). In this paper, we report on some aspects of stability of
a jet fuel prepared from Paraho shale oil.

    Previous work with shale oil derived middle distillates has
noted the very high freezing point of these fuels (3, 4, 1a). In
addition, shale oil fuels which were high in nitrogen gave as much
as 45% conversion of fuel bound nitrogen to NO_x emmissions when
burned under typical jet engine conditions (1d). The high nitrogen
content shale oil jet fuels were also found to form particulates
and gums upon standing at ambient temperatures in the absence of
light (3).

    Stablity of fuels concerns the tendency of fuels to form
particulates and/or coatings or deposits on engine surfaces under
two different sets of conditions. One set of conditions are those
of storage: temperatures of $\leqslant 40°C$, quiescent exposure to air, no
light. The other set of conditions are those which the fuel is
likely to encounter in a jet engine fuel system: temperatures in
the range 150-250°C, agitation in the presence of air, no light.
Shale oil derived fuels used in this work were significantly poorer
than petroleum derived fuels under both stability regimes and a
thorough study of the stability of these fuels was undertaken.

EXPERIMENTAL

    The shale oil derived jet fuel (designated Shale-I) used in this
work was produced from a crude shale oil (supplied by Paraho, Inc.) by
hydrotreatment at the Gary-Western refinery. The entire production
operation has been fully described elsewhere (1c). The physical prop-
erties of the jet fuel have been reported (1a).

    High temperature stability of the fuels was measured using an
Alcor, Inc. Jet Fuel Thermal Oxidation Tester (JFTOT) (5). Low tem-
perature (storage) stability was determined by measurement of gums,
contamination and peroxide concentration (all by ASTM standard methods)
before and after exposure to temperatures of 60°C for four weeks. The

fuels were stored in 1ℓ low actinic, dark pyrex glass bottles and were loosely covered to prevent exposure to airborne particulates. Air could still diffuse into the vessel. The vessels with fuel and various additives were thermostated at 60°C for the specified length of time.

Isolation of shale oil jet fuel basic nitrogen compounds was accomplished by acid extraction followed by neutralization of the HCl adducts (3). The basic nitrogen compounds thus obtained were analyzed by gas chromatography using a Perkin-Elmer model 3920B gas chromatograph equipped with a 100m OV-101 glass WCOT column and nitrogen-specific detector. This column separated the nitrogen compounds into at least 70 incompletely resolved components. Tentative identification of some of the components was made by combined gas chromatography-mass spectrometry (gc-ms) using a Hewlett-Packard model 5982 gc-mass spectrometer with a Hewlett-Packard model 5933A dedicated data system. The mass spectrometer was equipped with a 33m SE-30 SCOT column and was operated in the EI mode at 70 eV. In addition, the extracted basic nitrogen compounds were subjected to field ionization mass spectroscopy (FIMS). Ions produced by field ionization tend not to fragment and an accurate MW profile of a mixture can be constructed (6).

RESULTS AND DISCUSSION

Oil shale, as well as crude shale oil, typically smell of nitrogenous compounds. Early work with refined shale oil clearly showed (3) that the shale oil jet fuels used (∿1000 ppm nitrogen) were unstable and rapidly plugged filters upon standing for several days. Removal of nitrogenous material by acid extraction or by passing the fuel over clay or silica gel resulted in improved storage properties. The chemical constitution of the nitrogen containing materials was sought in an effort to discover specific classes of compounds which could cause stability problems. It is well-known that pyrroles and indoles are quite reactive toward air and light (7) and if present in large quantities in these fuels might account for the observed instability.

The Shale-I jet fuel contained 976 ppm nitrogen, of which 860 ppm nitrogen was acid extractable. The neutralized extract was subjected to gas chromatography using an all glass system with high efficiency capillary column. A chromatogram of the acid extract obtained using a nitrogen specific detector is shown in Figure 1. As shown, retention time matching implies that the majority of compounds are pyridine-type bases. The mixture was also subjected to gc-mass spectroscopy. The total ion chromatogram is shown in Figure 2. The lower resolution SCOT column used on the mass spectrometer did not permit unequivocal assignment of each peak. Tentative assignments of the numbered peaks are noted in Table I. In many cases, the electron impact mass spectrum clearly showed the presence of more than one compound. However, the main compound type observed was alkyl substituted pyridine with lesser quantities of quinolines. We used another mass spectral technique to help confirm our gc-ms assignments. The FIMS results are tabulated in Table II. Since molecules tend not to fragment when field ionized, the FIM spectrum can be scanned for parent masses and compound classes and higher alkyl substituted homologs readily recognized. The FIMS data confirms the presence of major amounts of pyridine compounds with lesser quantities of quinoline and tetrahydroquinoline types. Significantly, indoles and pyrroles are present only in very small amounts. While ionization efficiencies for various classes of compounds under

FI conditions are not known with certainty we do not expect them to be very different for the aromatic nitrogen types observed here. We have observed that FIMS data on basic nitrogen compounds results in a higher than expected intensity for parent +1 peaks. This was observed for our basic nitrogen extracts but not for n-alkane or neutral fuel samples. We attribute this phenomenon to the presence of water in the basic nitrogen extracts; the water rapidly protonates the radical cation generated by FI.

Extraction of the Shale-I jet fuel with HCl is approximately 90% efficient for removal of nitrogen containing material. Remaining in the fuel are 116 ppm of non-basic nitrogen compounds. Presumably, these compounds will be comprised primarily of pyrrole, indole and carbazole types. Only traces of substituted pyrroles and indoles were observed by FIMS in the basic nitrogen fraction (Table II). Shale oil nitrogen compounds have been characterized previously (8) and since carbazoles and pyrroles could not be titrated it is not surprising that they are also not efficiently extracted by lN HCl.

High Temperature (Thermal) Stability - The high temperature stability of the Shale-I jet fuels was measured using the JFTOT technique (5). The thermal oxidative stability of the received fuel (976 ppm N) was measured. The fuel was then acid extracted, the isolated basic nitrogen compounds added back into the extracted shale fuel in varying quantity, and the thermal oxidative stability redetermined. A petroleum derived JP-5 was also subjected to JFTOT testing. The petroleum fuel had a breakpoint temperature of 275°C and at 260°C did not produce significant TDR readings or develop a significant pressure drop across the in-line JFTOT filter. A number of nitrogen compounds, typical of those found in this study, were then added to the petroleum derived JP-5 and the high temperature stability redetermined. The results with shale and petroleum fuels are displayed in Table III.

In previously reported stability work with shale oil derived jet fuels (9) it was shown that the JFTOT thermal stability of shale oil derived fuels increased with decreasing total nitrogen content of the fuels. In Table III, it is observed that the thermal stability of the Shale-I fuel increases as the concentration of basic nitrogen compounds decreases. In previous work (9) the lower nitrogen contents of the shale oil jet fuels were achieved by more severe hydrotreatment. It can also be observed that there apparently are two major modes of high temperature thermal instability and the effect of basic nitrogen is different in each. If thermal stability by JFTOT is measured only by tube deposits, then for the Shale-I fuel a slight rise in breakpoint temperature is observed as the basic nitrogen content is reduced (breakpoint by TDR from 244°C to 254° as basic N changes from 838 to 7 ppm). However, if the filter pressure drop is used for determining breakpoint then a much larger change, 227 to 279°C in breakpoint temperature, is observed as basic nitrogen content is reduced.

In order to confirm some of the effects of nitrogen compounds on high temperature stability, pure compounds which are similar to those found in the Shale-I basic nitrogen fractions (Tables I and II) were added to a petroleum based jet fuel of high stability (Table III). Most of the basic nitrogen compounds used resulted in negligible deposit (TDR) formation with the exception of 2-amino-3-methylpyridine. 4-t-Butylpyridine showed evidence of filter plugging but little TDR

deposits were formed. Pyrrole, however, was found to produce a very high deposit rating (TDR) and also plugged the in-line filter. Much more work with pure compounds in simple carrier vehicles is necessary before definitive mechanistic inferences can be drawn regarding the effects of the various classes of nitrogen compounds.

Storage Stability - The low temperature or storage stability of the Shale-I fuel was followed by determining changes in peroxide concentration, gum and contamination levels and changes in high temperature stability (JFTOT behavior). The latter method was employed since deposit precursors, which might form at low temperatures, could seriously degrade engine operation if present in sufficient concentration. The test fuel was placed in 1ℓ glass bottles which were loosely covered to permit air diffusion to the fuel. Ten ml of distilled water and 1 g of iron fillings were placed in each sample. These conditions simulated actual storage tank conditions since water is always present in fuel storage tanks and the fuel is in contact with usually uncoated metal surfaces of storage tanks. The samples were maintained at 60°C for four weeks. The results of the storage stability experiments are presented in Table IV.

Storage stability measurements have been performed on some shale derived fuel (10). In that study, a Paraho jet fuel (very similar to our Shale-I) was found to form some gums (increase in gums of about 2 mg/100 ml fuel after 32 weeks storage at 43°C) but there was only a small increase in acid number and no increase in viscosity. In our storage tests, we tried to determine the effects of basic nitrogen compounds on the storage stability of the Shale-I fuel. The combination of acid extraction followed by silica gel chromatography of the Shale-I fuel was found to be effective for removing all nitrogen containing compounds. The nitrogen free Shale-I showed some tendency to accumulate peroxides under our test conditions, but no appreciable gums were formed. In addition, the high temperature (JFTOT) stability of the aged nitrogen-free fuel was similarly acceptable (Table IV). Increasing quantities of basic nitrogen compounds, which were acid extracted from the fuel, were then reintroduced into the fuel and the storage stability redetermined. It will be noted that as the concentration of basic nitrogen compounds increases from 8.4 to 125 ppm N, both the gum content and peroxide concentration after storage rise to a maximum (25 ppm N) then fall back to lower levels (Table IV, expt. #2, 3, 4). However, the JFTOT deposit rating after storage was monotonically degraded by increasing nitrogen levels. The results imply a relationship between gum formation and peroxide concentration. It is possible that the relation between the gum and peroxide is of the form:

$$RH \xrightarrow[k_1]{O_2} [peroxide] \xrightarrow{k_2} gum$$
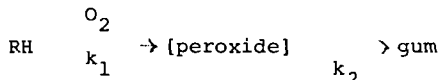
Fuel hydroperoxides are known to be stable to temperatures of approximately 250°C (11). However, hydroperoxides can react at mild conditions to attack some rubbers. We propose that some fuel components, particularly those containing sulfur, nitrogen, oxygen, and olefinic functional groups, also react under storage conditions with peroxides. Condensation or dimerization of the free radical intermediates formed in these

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reactions can build the highly polar, medium molecular weight (400-500) gums observed in some studies (12). Antioxidants of either the phenylene diamine or hindered phenol type were effective for inhibiting both peroxide and gum formation in the current studies (Table IV, expts. #5, 6, 8).

A pyridine compound was found to storage degrade the Shale-I fuel faster than a pyrrole compound (Table IV, expt. #9,11). After storage the Shale-I fuel doped with 50 ppm 5-ethyl-2-methylpyridine had an order of magnitude more gums and 20 times the peroxide level compared to the same fuel containing 50 ppm 2,5-dimethylpyrrole after storage. Antioxidants were effective at inhibiting both gums and peroxides in the nitrogen doped fuels after storage (Table IV, expt. #10, 12). 5-Ethyl-2-methylpyridine caused a large decrease in JFTOT results after storage (TDR reading from four prior to storage to 35 after storage). In contrast, 2,5-dimethylpyrrole caused equally poor JFTOT performance before and after storage.

SUMMARY

High temperature thermal stability and storage stability experiments were conducted using Shale-I jet fuel. As basic nitrogen compounds are removed by acid extraction from the Shale-I fuel, JFTOT stability improves (especially filter pressure drop performance). After four weeks of accelerated storage, the Shale-I fuel containing basic nitrogen compounds formed more gums and peroxides, and exhibited degraded JFTOT performance. The basic nitrogen compounds extracted from the Shale-I fuel were characterized by way of various mass spectral methods. Compounds similar to those found in the basic nitrogen fraction were used as additives for JFTOT and storage tests on a petroleum fuel and nitrogen-free Shale-I fuels. Both pyridines and pyrroles evidence participation in unstable behavior. Much more work must be performed in order to establish clear trends and to deduce a detailed mechanism of fuel degradation.

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TABLE I. Tentative Structural Assignments of GC-MS Peaks

Peak #[A]	Prominent Peaks m/e (Peak, Rel. Abundance)	Tentative Assignment
1	78(M^+, Base),77(M^+-1,20%),52(15%)	benzene
2	107(M^+,Base),106(M^+-1,50%),92(M^+-CH_3,20%),79(M^+-HCN,30%)	4-ethylpyridine
3	121(M^+,40%),120(M^+-1,Base),107(M^+-CH_2,25%),93($M^+-C_2H_4$,20%)	2-methyl-ethylpyridine
4	121(M^+,Base),120(M^+-1,30%),106(M^+-CH_3,21%),79($M^+-C_3H_6$,35%)	4-i-propyl pyridine
5	121(M^+,85%),120(M^+-1,Base),107(M^+-CH_2,25%),93($M^+-C_2H_4$,15%),79($M^+-C_3H_6$,35%)	2-propylpyridine
6	121(M^+,Base),120(M^+-1,55%),106(M^+-CH_3,50%),93($M^+-C_2H_4$,15%)	3-ethyl-4-methylpyridine
7	135(M^+,45%),134(M^+-1,Base),121(M^+-CH_2,45%),107($M^+-C_2H_4$,25%),106($M^+-C_2H_5$,30%)	2-propyl-methylpyridine
8	135(M^+,Base),134(M^+-1,55%),121(M^+-CH_2,20%),120(M^+-CH_3,50%)	3,4-diethylpyridine
9	135(M^+,45%),134(M^+-1,Base),121(M^+-CH_2,30%),120(M^+-CH_3,35%),107($M^+-C_2H_4$,65%)	2-propyl-methylpyridine
10	135(M^+,Base),134(M^+-1,75%),121(M^+-CH_2,15%),120(M^+-CH_3,30%),107($M^+-C_2H_4$,28%),106($M^+-C_2H_5$,30%)	4-butylpyridine
11	149(M^+,15%),148(M^+-1,33%),135(M^+-CH_2,33%),134(M^+-CH_3,56%),121($M^+-C_2H_4$,Base)	3-propyl-4-ethylpyridine
12	163(M^+,6%),162(M^+-1,11%),149(M^+-CH_2,53%),148(M^+-CH_3,40%),121($M^+-C_3H_6$,Base)	3-propyl-4-ethyl-5-methylpyridine
13	163(M^+,8%),162(M^+-1,15%),149(M^+-CH_2,60%),148(M^+-CH_3,Base),134($M^+-C_2H_5$,44%),121($M^+-C_3H_6$,30%)	3-ethyl-4-butylpyridine
14	163(M^+,25%),162(M^+-1,55%),149(M^+-CH_2,34%),148(M^+-CH_3,55%),135($M^+-C_2H_4$,Base)	2-propyl-3-methyl-4-ethylpyridine
15	163(M^+,9%),162(M^+-1,25%),148(M^+-CH_3,18%),134($M^+-C_2H_5$,30%),121($M^+-C_3H_6$,Base)	2-butyl-4-ethylpyridine
16[B]	163(M^+,27%),162(M^+-1,20%),147(45%),121($M^+-C_3H_6$,Base)	3,4-dipropylpyridine + tetrahydro-methyl quinoline
17[B]	176(M^+-1,11%),163(M^+-CH_2,30%),162(M^+-CH_3,37%),147(M^+,80%),146(70%),143(M^+,Base)	C_7-pyridine + 3-methylquinoline + tetrahydromethyl quinoline

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TABLE I – continued

Peak #[A]	Prominent Peaks m/e (Peak, Rel. Abundance)	Tentative Assignment
18[B]	Complex spectrum	probable species include C_6-pyridine, C_1-quinoline, methyl-tetrahydroquinoline, ethyl tetrahydroquinoline
19[B]	$177(M^+,6\%),176(M^+-1,10\%),162(M^+-CH_2,18\%),161(M^+,18\%),135(M^+-C_3H_6,Base)$	probable components: C_7-pyridine (one butyl group), ethyl-tetrahydroquinoline, methyl tetrahydroquinoline, methylquinoline
20[B]	$177(M^+,8\%),176(M^+-1,15\%),160(M^+-1,15\%),134(M^+-C_3H_7,26\%),121(M^+-C_4H_8,Base)$	major: C_7-pyridine (with 2-pentyl gp)
21[B]	Complex spectrum	probable major components: C_2-quinoline, C_2-tetrahydroquinoline; minor: C_7-pyridine
22[B]	Complex spectrum	probable major components: C_2-quinoline; minor components: C_2-tetrahydroquinoline, C_7-pyridine; trace:C_4-tetrahydroquinoline
23[B]	Complex spectrum	probable major component: C_8-pyridine; very minor components; C_2-quinoline, C_2-tetrahydroquinoline
24[B]	$191(M^+,14\%),190(M^+-1,5\%),171(M^+,45\%),170(M^+-1,25\%),121(M^+-70,Base)$	major: C_8-pyridine, C_3-quinoline; minor: C_2-quinoline, C_2-tetrahydroquinoline
25[B]	$171(M^+,Base),170(M^+-1,30\%),156(M^+-CH_3,25\%),149(25\%)$	3-methyl-4-ethyl quinoline; minor: C_8-pyridine, other quinoline types
26[B]	Complex spectrum	probable major components: C_9-pyridine, C_3-quinoline
27[B]	Complex spectrum	probable major components: C_9-pyridine + C_3-quinoline

[A,] Refer to Figure 2 for numbered peak position in total ion chromatogram of gc-mass spectrum. [B,] EI spectra showed evidence of more than one compound.

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TABLE II. Field Ionization Mass Spectrum
Base Fraction from Shale-I JP-5

Series	Range of "n" Values*	Compounds	Relative Ion Count
$C_nH_{2n+1}N$	7 - <u>12</u> - 14	Piperidines	10
$C_nH_{2n-3}N$	7 - <u>9</u> - 15	Pyrroles	28
$C_nH_{2n-5}N$	7 - <u>9</u> - 16	Pyridines	1000
$C_nH_{2n-7}N$	9 - <u>11</u> - 16	Tetrahydro-quinolines	170
$C_nH_{2n-9}N$	8 - <u>13</u> - 15	Indoles	13
$C_nH_{2n-11}N$	9 - <u>11</u> - 14	Quinolines	157

* Underlined value of "n" indicates components in largest amount.

TABLE III. High Temperature Stability of Jet Fuels [A]

Fuel Type	Organic Nitrogen, ppm		Breakpoint Temperature, [B] °C	
	Acid Extractable	Total	Heater Tube (TDR)	Filter
Shale Oil–Jet Fuel	860	976	-	232
	838[C]	954[C]	244	227
	97[C]	213[C]	243	232
	50[C]	166[C]	251	241
	7[C]	123[C]	254	279

Petroleum[D]	Additive Conc., ppm	260°C Max TDR	260°C ΔP, mm
	4-t-butylpyridine, 56	1	20
	2-t-butylpyridine, 49	10	1
	5-ethyl-2-methylpyridine, 107	11	3
	4-benzylpyridine, 56	7	2
	2-amino-3-methylpyridine, 134	45	14
	N,N-dimethylaniline, 82	6	5
	pyrrole, 100	32	Bypass[E]

[A], Measured using Alcor, Inc. JFTOT according to ASTM Standard Method D-3241. [B], Breakpoint is defined as the temperature of test at which a maximum TDR of >17 is observed or a pressure drop of >25 mm Hg is attained across the in-line JFTOT filter. [C], Shale Oil JP-5 extracted with HCl, washed, and the isolated basic nitrogen compounds reintroduced to the shale oil fuel. [D], The petroleum derived jet fuel had a breakpoint temperature of 275°C and had negligible TDR or filter pressure drop at 260°C. [E], Pressure drop of >25mm developed after which the test continued for standard 2.5 hr. period with the hot fuel bypassing the filter.

TABLE IV. Results of Storage Stability Tests of Treated Shale-I JP-5[A]

Sample (Expt.#)	N-Additive, ppm[C]	Inhibitor, ppm[B]	Existent Gums, mg/100 ml		Contamination, ppm		Peroxide, meq/kg		JFTOT 260°C Max TDR	
					Storage Results					
			Before	After	Before	After	Before	After	Before	After
Treated Shale-I (1)	0	0	0	0	0	0	0.14	60	1	10
" (2)	8.4	0	0	1.4	1.4	2.4	1.4	64.3	9	13
" (3)	25	0	0	5.4	0.9	1.7	1.0	96.8	4	27
" (4)	125	0	0	1.6	0.9	2.0	0.2	42.5	5	48
" (5)	0[D]	25-DA	0	0	0	0.8	0	1.0	0	2
" (6)	39[D]	25-DA	0	0	0	1.8	0	0.6	0	2
" (7)	123	25-DA	0	0	0.7	2.0	0.1	0.1	5	13
" (8)	0	24-HP	0	0	-	-	0.7	0.7	4	9
" (9) 5-ethyl-2-methylpyridine, 50		0	0	5	-	-	0.6	83	4	46
" (10)	"	24-HP	0	5	-	-	0.6	0.6	4	35
" (11) 2,5-dimethylpyrrole, 50		0	0	0.4	-	-	0.6	4.2	25	25
" (12)	"	24-HP	0	0.6	-	-	0.6	0.5	26	25

[A] Shale-I JP-5 containing 976 ppm nitrogen was first acid extracted then treated with silica gel to yield a nitrogen-free fuel. Conditions of storage test: temp=60°C; time=4 weeks; no agitation; air allowed to freely diffuse into fuel.
[B] Antioxidants used were commercial products qualified for Navy fuel use; DA=phenylene diamine (1,4-diamino benzene); HP=hindered phenol (2,6-di-tert-butyl-4-methylphenol). [C] Acid extracted nitrogen compounds added to nitrogen-free Shale-I JP-5 to bring nitrogen content to designated level. [D] Corrected for antioxidant nitrogen content.
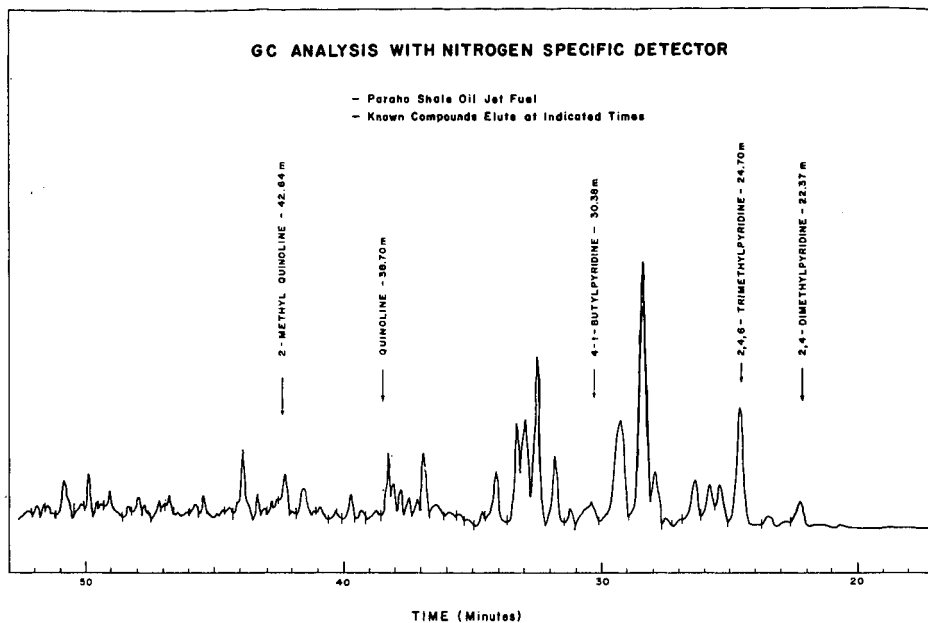
Fig. 1.   Gas Chromatogram of Shale-I basic nitrogen compounds
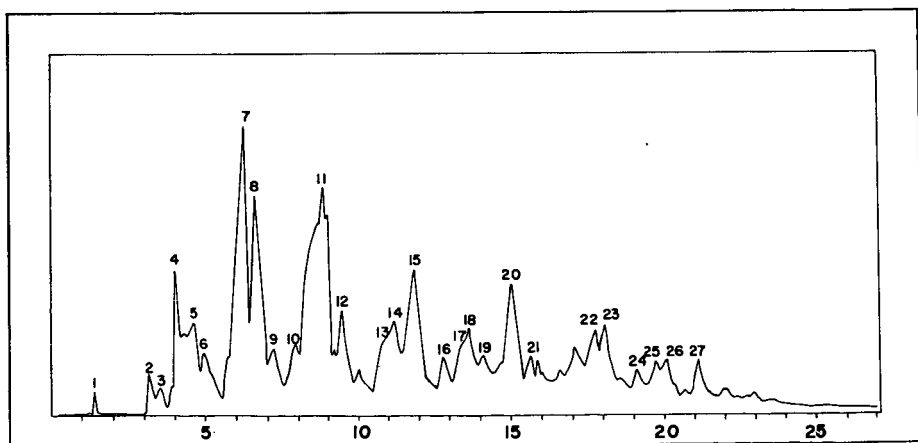   using a 100m OV-101 WCOT column.

Fig. 2.   Total Ion Chromatogram of Shale-I basic nitrogen fraction.

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